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TUNNELING AND POINT CONTACT SPECTROSCOPY OF HIGH-T_c SUPERCONDUCTING THIN FILMS

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Tunneling and point contact junctions between a normal metal and thin high temperature superconducting film were studied to obtain information on surface properties. Surface degradation and time development of contact resistance are investigated as well as peculiarities of the conductance–voltage characteristics. The quasi-linear background is related to carrier transport through degraded surface layer described by a model of inelastic scattering from a broad flat continuum of states inside the potential barrier. An asymmetry of the characteristics appears as the result of low Fermi energy values in the high temperature superconductors in comparison to common metals. An extrinsic nature of these peculiarities is supported by effects of barrier formation by applied voltages in the 1 volt range. As an often observed anomaly a conductance peak at zero bias is observed which can be related to different mechanisms. In the case of high temperature superconductors this zero bias anomaly is related to the *d*-wave pairing symmetry of the pair potential. Experimental results on YBCO and BSCCO films are compared to calculations taking into account the Andreev reflections for a junction between a normal metal and a *d*-wave superconductor.

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1. Introduction

Since the discovery of high-T_c superconductors (HTS) a lot of effort has been made to study their basic physical properties. One of the most powerful methods for such study is the tunneling spectroscopy which directly probes correction to normal density of states caused by many-body effects [1]. Although the tunneling spectroscopy gives good agreement with theory for low temperature superconductors the tunneling spectra obtained on HTS exhibit a lot of peculiarities which are not satisfactorily explained by the theory. The most often and reproducibly observed peculiarities are linear background (LB) and conductance peak at zero bias voltage (the so-called zero bias anomaly — ZBA). LBs have been already observed on nonsuperconducting systems and were ascribed to transport mechanisms as inelastic tunneling [2], tunneling through localized states [3]. On the other hand several theoretical models as resonance-valence-band (RVB) [4] and marginal-Fermil-liquid theory [5] suppose that LB is an intrinsic property of HTS. Likewise ZBA can be caused by transport mechanism as Kondo effect [1], Josephson effect [6] or be a consequence of bound states arisen on the surface of *d*-wave superconductors [7]. Thus a question arises whether LB and ZBA are intrinsic properties of HTS or are rather caused by transport mechanisms. In the next sections we address the above question.

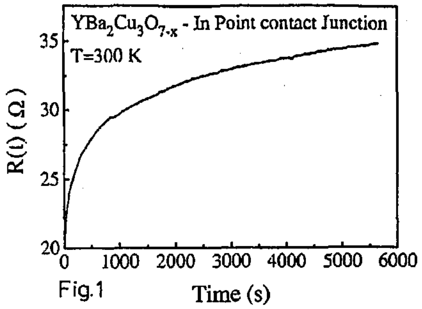
2. Experimental

The measurements of $I-V$ and $\mathrm{d}V/\mathrm{d}I$ vs. V characteristics were carried out on $YBa_2Cu_3O_{7-x}$/normal metal (Au, In) and $Bi_2Sr_2CaCu_2O_{8+y}$/Au point contact and planar junctions. The YBaCuO and BSCCO thin films were prepared by laser ablation on $SrTiO_3$ substrate [8, 9]. Point contact junctions at various temperatures ($4.2 \div 300$ K) were prepared. For preparation of planar junctions a classical lift-off technique was used. An upper electrode (Au) was evaporated *ex situ*. In such junctions we observed an increase in point contact resistance and influence of external bias voltage on properties of HTS/metal interface. The measurements on various types of contacts and various HTS materials give some evidence that experiments described below do not depend on a type of contact or material.

$I-V$ characteristics were measured by a standard four-point computer controlled technique. $\mathrm{d}V/\mathrm{d}I$ vs. V characteristics were taken using ac conductance bridge with low frequency modulation (≈ 780 Hz). $\mathrm{d}I/\mathrm{d}V$ vs. V characteristics were obtained by numerical inversion of $\mathrm{d}V/\mathrm{d}I$ vs. V characteristics.

3. Degradation processes in the surface layer

The main problem of tunneling spectroscopy of HTS is preparation of good HTS/metal or HTS/insulator interface without structural defects as oxygen vacancies, inhomogeneities, etc. Degradation processes in surface layer of HTS hinder one to prepare the good interface and consequently to prepare a defined tunnel junction. Degradation processes in surface layer of HTS were studied in contact with metal (Pb [10], Au [11]), air and humidity [12]) as well as in vacuum [13]. In all cases a loss of oxygen from upper layer of HTS (with thicknesses $0.4 \div 4$ nm) was documented. Oxygen content in HTS considerably influences their superconducting properties. Moreover the surface layer determines properties of superconducting weak link prepared on the base of HTS because of the small coherence length of HTS (e.g. $\xi_c \simeq 0.3$ nm and $\xi_{ab} \simeq 1.5$ nm for $YBa_2Cu_3O_{7-x}$). An influence of degraded surface layer on superconducting energy gap Δ_0 was documented in Ref. [14]. A dependence of the value of energy gap on temperature of point contact preparation was found. The maximal value of $\Delta_0 = 30$ meV was measured on the point contacts prepared at a temperature of $T = 4.2$ K however for point contacts prepared at room temperature the maximal value of energy gap achieves $\Delta_0 = 20$ meV only. It was explained (and confirmed by XPS spectroscopy) by degradation processes in HTS near the interface. This suggestion was supported by measurement of time evolution of point contact resistance. In Fig. 1 an increase in point contact resistance immediately after preparation is shown. This change was explained in the term of out-diffusion of oxygen from surface layer of HTS near HTS/metal interface caused by lower activation energy of oxygen on the surface [15]. On the base of our results we assume the lowering of the surface barrier for out-diffusion of oxygen from HTS due to Schottky effect. This assumption is also supported by influence of external bias voltage on the change of point contact resistance (see Fig. 2) immediately after its preparation. Whereas oxygen ions are negatively charged an external bias voltage changes the surface barrier and out-diffusion of oxygen is suppressed or enhanced depending on polarity of the bias voltage.



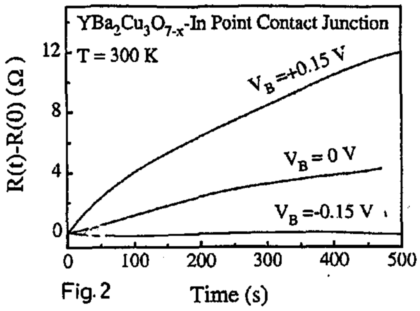


Fig. 1. Time dependence of change in point contact resistance of a YBCO/In junction at a temperature of $T = 300$ K.

Fig. 2. Time dependence of the point contact resistance of a YBCO/In junction on the same point contact after application of external bias voltage -0.15 V, 0 V and +0.15 V.

An application of higher external bias voltage comparable with activation energy of oxygen diffusion ($E_a \approx 1$ eV) leads to next interesting results. We investigated $I-V$ characteristics and their derivatives in $YBa_2Cu_3O_{7-x}$/normal metal point contact and planar junctions in the voltage range up to ±2 V. In $I-V$ characteristics measured on these junction we observed either an increase in junction resistance above voltage V_a if positive bias voltage related to metal electrode was applied (Fig. 3, change from curve with open circles to curve with full circles at positive voltages) or a decrease in junction resistance if negative voltage above $-V_a$ was applied (Fig. 3, curve with full circles changes to curve with open circles at negative voltages). Figure 4 gives the differential conductivity corresponding to the curves of Fig. 3 showing the change from linear to quadratic background. Similar results on the $YBa_2Cu_3O_{7-x}$/metal (for $x = 0.3$ and 0.63) and $Y_{1-a}Pr_aBa_2Cu_3O_{7-x}$/metal (for $a = 0.2$ and 0.4) point contact junctions were obtained [16].

The changes started above voltage V_a and below $-V_a$ which correlate with activation energy of oxygen in CuO layer of YBCO unit cell, i.e. $\pm 0.5\ \mathrm{V} \div \pm 2\ \mathrm{V}$. This effect we explained by rapid changes of oxygen concentration in HTS near

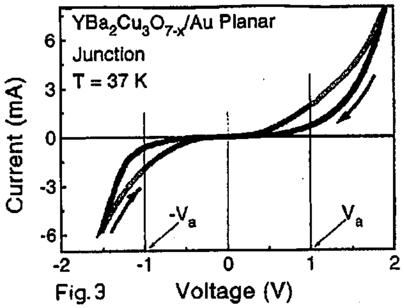


Fig.3

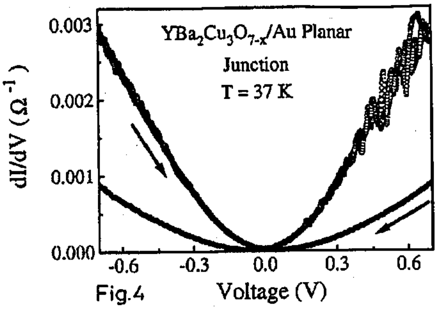


Fig.4

Fig. 3. $I-V$ characteristics measured on $YBa_2Cu_3O_{7-x}$/Au planar junction at a temperature of $T = 37$ K. These changes are reproducible several times on the same contact. In this figure three characteristics measured on the same junction are shown. These characteristics are identical.

Fig. 4. Derivatives of three $I-V$ characteristics from Fig. 3 in the voltage range of ±0.5 V. All three characteristics (three for linear background (opened circles) and three for quadratic background (solid circles)) are identical.

HTS/metal interface caused by the electric field or/and electromigration. The changes of oxygen content directly yield a change of resistivity in HTS near the interface [15, 17, 18].

These results indicate a possibility to change the quality and sharpness of the YBCO/metal interface. An influence of the above-mentioned changes on differential conductance of tunneling junction will be described below.

4. Tunneling across a degraded surface layer

On the surface of HTS the so-called native barrier is always created. The suggestion that this barrier is created from a degraded surface layer of HTS is commonly accepted. However under the native barrier the oxygen depleted layer must exist which plays a crucial role in formation of HTS/metal junction. It is well known that most HTS are doped with antiferromagnetic insulator where antiferromagnetic correlations within the CuO_2 planes persist up to fully oxygenated $YBa_2Cu_3O_7$. Moreover in the oxygen depleted layer a long-range antiferromagnetic ordering exists and in this layer spin fluctuations can play the role of effective scattering centers and therefore influence the tunneling conductivity of HTS/metal tunneling junction.

4.1. Linear background

As was shown in Sec. 3 the energy $\pm eV_a$ correlates with the activation energy of oxygen in CuO planes in the YBCO unit cell thus we explain an increase and decrease in junction resistance due to the movement of oxygen in CuO plane from the stationar to the interstationar position and vice versa (due to the field effect or/and electromigration) with respect of applied bias voltage polarity. Due to the change of oxygen content in the surface layer of YBCO we change the carrier concentration in CuO_2 planes and thus we increase or destroy the long-range

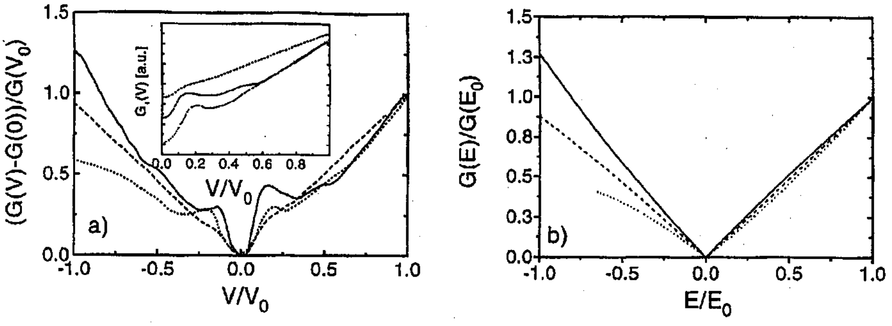


Fig. 5. (a) Normalized differential conductivity measured on YBaCuO/Au point contact junctions with various phases of YBaCuO ($T_c \approx 90$ K and $E_F \approx 0.25$ eV — solid line, $T_c \approx 60$ K — dashed line) and LSCO/Pt ($T_c \approx 36$ K and $E_F \approx 0.1$ eV — dotted line) measured at a temperature of 4.2 K. Differential conductivity of LSCO/Pt point contact represents the experimental data of Kirtley et al. [30]. The inset: Even part of the conductivity $G_+(V) = [G(V) + G(-V)]/2$. (b) Theoretical curves of inelastic differential conductivity for $\eta = 0$ with the tunneling barrier parameters $\overline{\phi} = 0.75$ eV, $d = 11$ Å (that correspond to $E_0 \approx 0.15$ eV) and various values of the Fermi energy $E_F = 0.25$, 0.15, 0.1 eV (from the top to the bottom, respectively) calculated from the relation (2).

antiferromagnetic order in these layers. Thus by high bias voltage we can increase or decrease the number of inelastic scattering centers (magnons) in YBCO surface layer. Really in the voltage range ±0.7 V derivatives of $I-V$ characteristics show the linear or quadratic background (depending on the history of the recording of $I-V$ characteristics).

The quadratic background is typical of tunneling junction with the well-defined barrier and good interface [19]. In other case we explained the linear background by inelastic scattering of tunneling quasiparticles in the barrier due to the existence of long-range antiferromagnetic spin fluctuations in the barrier [20, 21]. It is in full agreement with Kirtley's model of inelastic transport through the HTS/metal interface [22]. Also asymmetry of the differential conductivity corroborates that inelastic tunneling is dominant. As one can see from Fig. 5a the asymmetry is positive (i.e. $G(|V|) > G(-|V|)$) for HTS with high Fermi energy but negative for HTS with low Fermi energy. Nevertheless the even part of differential conductivity, $G_{\mathrm{even}}(V) = (G(|V| + G(-|V|)/2$, is a linear function of bias voltage for all HTS investigated. The theoretical analysis has shown that differential conductivity for inelastic tunneling can be expressed as [23]

$$G_i(V) \sim E_0 \left[\exp\left(\frac{E_F}{\mathrm{E}_0}\right) - 1\right] |qV| + \frac{1}{4}\left[(3 - 2\eta) - (1 - 2\eta)\exp\left(\frac{E_F}{\mathrm{E}_0}\right)\right] |qV|qV, \tag{1}$$

where E_F is the Fermi energy of HTS, $E_0 = \overline{\phi}/(\kappa_0 d)$, $\kappa_0 = \sqrt{2m\overline{\phi}/\hbar^2}$, $\overline{\phi}$ is the height of rectangular barrier, d is the width of barrier, $\eta = (d - d_1)/d$ and d_1 is the distance between HTS and plane where the inelastic scattering takes place. In real experiment it is expected that the most oxygen deficient layer of HTS is just on its surface, and thus $\eta \to 0$. The comparison of theoretical results for $\eta = 0$ with experimental ones gives good agreement (see Fig. 5). On the basis of our results we can conclude that linear background is not an intrinsic property of HTS materials.

5. Zero bias anomaly

Already in the early tunneling measurements on HTS, a peak of the conductance around zero voltage was sometimes observed. The understanding of these zero bias anomalies in 1992 has been reviewed by Walsh [24]. The most important observation was that ZBA is connected to the superconducting state of HTS; its magnitude decreases with increasing temperature and it disappears above T_c of HTS, while it still exists above T_c of the counterelectrode.

Theoretically it was shown that the existence of ZBA can be explained by several models but the most promising are the following:

1. Appelbaum–Anderson model assumed the existence of localized spin moments inside the tunnel barrier [25],
2. midgap state in *d*-wave superconductors [7].

Let us confront our as well as other experimental results with the above models. Many authors ascribe the ZBA to spin-flip scattering of tunneling quasiparticles by localized spins in the tunnel barrier. To be concrete the Kondo tunneling process in which one electron is reflected and the second is transmitted through the tunnel barrier by spin-flip scattering leads to considerable ZBA [25]. This is caused by the fact that only a small part of quasiparticles is transmitted through the barrier and the Kondo scattering opens an additional tunneling channel. The main argument for this explanation is the fact that the Zeeman splitting of the ZBA into two peaks was observed by the application of external magnetic field. However this theory has a lot of problems to explain other experimental facts. At first the experiments imply large and magnetic-field dependent *g*-factors [26]. In addition for junction with direct conductivity the Kondo scattering should lead to the dip in contradiction with our experiment. The reason is the same as the one given in Ref. [27]: for a large strength of the tunnel barrier $Z > 1$ the interaction of tunneling electron with some excitation in the barrier leads to an increase in conductance and for $Z < 1$ to a decrease. As one can see from Fig. 6 the zero bias conductance peak (ZBCP) is still visible for the point contact with the small parameter of Z ($Z < 1$). Within this model there are also problems to explain why ZBA diminishes above T_c as the Kondo effect has no connection with superconductivity.

The most promising explanations of ZBA are those considering the existence of bound states on the surface of *d*-wave superconductors [7]. It was found that for some orientation of *d*-wave superconductor zero bias conductance peak appears in conductance spectrum because of the dependence of Andreev reflection on the phase of pair potential [28]. In Fig. 6 one can see a comparison of our experimental data obtained on HTS/metal point contacts with theoretical curves calculated from the theory for *d*-wave superconductor/metal point contact [28].

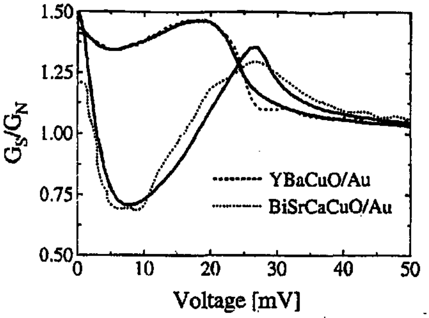


Fig. 6. Ratio of conductivity in the superconducting and normal conducting state versus voltage measured on YBaCuO/Au and BiSrCaCuO/Au point contacts at a temperature of 4.2 K (dashed and dotted lines) are fitted by the theory valid for d-wave superconductor/metal contact (solid lines) [28] with the fitting parameters $\Delta = 24$ meV, $Z = 0$ for YBaCuO and $\Delta = 28$ meV, $Z = 0.85$ for BiSrCaCuO for parameters $\lambda_0 = k_{\mathrm{Fs}}/k_{\mathrm{Fn}} = 0.7$, $r = v_{\mathrm{gs}}/v_{\mathrm{gn}} = 0.4$ and $\beta = 10$. The k_{Fs}, v_{gs} and k_{Fn}, v_{gn} are wave vectors and group velocities in HTS and metal, respectively.

According to this theory the normalized conductivity of S/N point contact can be expressed in the form

$$\sigma(E) = \frac{\int_{-\pi/2}^{\pi/2} \mathrm{d}\Theta \sigma_s(E,\Theta) \exp(-\beta\Theta^2) \cos\Theta}{\int_{-\pi/2}^{\pi/2} \mathrm{d}\Theta \sigma_n(E,\Theta) \exp(-\beta\Theta^2) \cos\Theta}, \tag{2}$$

where σ_s, σ_n are given in Ref. [28] and the term $\exp(-\beta\Theta^2)$ characterizes the directionality of the "tunneling" process resulting from non-zero thickness of the barrier (see [1, 29]) or the special geometry of the experiment (point contact). The agreement between experimental and theoretical results is excellent and gives some evidence for d-wave pairing in HTS.

6. Conclusion

We have studied the influence of external bias voltage on HTS/metal junction properties. We have found that it is possible to change the background of differential conductance characteristics from linear to quadratic and vice versa. In addition we have observed the asymmetry of differential characteristics of HTS/metal tunnel junctions for HTS with different Fermi energies. Both these effects were explained by inelastic tunneling through degraded surface layer of HTS. For HTS/metal junctions without degraded surface layer we observed differential characteristics corresponding to metallic regime, i.e. $Z < 1$. Differential characteristics exhibit a zero bias conductance peak which can be naturally explained by the existence of bound states on the surface of d-wave superconductor. Thus we can conclude that linear background is not an intrinsic property of HTS but it is rather connected with inelastic tunneling. On the other hand our results give some evidence that the zero bias conductance peak is an intrinsic surface property of HTS as d-wave superconductor.

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